

Z/RPS.

10/521612
DTo Rec'd PCT/PTO 14 JAN 2005
PCT/DK2003/000497

WO 2004/007789

Title: Case-hardening of stainless steel

Technical Field

- 5 The present invention relates to a method according to the preamble of claim 1, and a stainless steel article according to claim 11.

Background Art

- 10 Thermo-chemical surface treatments of steel by means of carbon or nitrogen carrying gases are well-known processes, called case-hardening or carburization or nitriding. Nitro-carburization is a process in which a gas carrying both carbon and nitrogen is used. These processes are traditionally applied to improve the hardness and wear resistance of iron and low alloyed steel articles. The steel article is exposed to a
15 carbon and/or nitrogen carrying gas at an elevated temperature for a period of time, whereby the gas decomposes and carbon and/or nitrogen atoms diffuse through the steel surface into the steel material. The outermost material close to the surface is transformed into a layer with improved hardness, and the thickness of this layer depends on the treatment temperature and the treatment time.

20

- Stainless steel has excellent corrosion properties, but is relatively soft and has poor wear resistance, especially against adhesive wear. Therefore, there is a need of improving the surface properties for stainless steel. Gas carburization, nitriding and nitro-carburizing of stainless steel involve some difficulties, as the passive layer, causing the good corrosion properties, acts as a barrier layer preventing carbon and/or nitrogen atoms from diffusing through the surface. Also the elevated temperatures of the treatments promote the formation of chromium carbides or chromium nitrides. The formation of chromium carbides and/or chromium nitrides reduces the free chromium content in the material whereby the corrosion properties are deteriorated.

25
30

process can be carried out at temperatures below 400°C, and the purpose is to obtain a pore-free iron nitride layer.

Disclosure of Invention

5

The object of the invention is to provide a new and improved method for case-hardening stainless steel. The object of the invention is obtained by a process according to the preamble of claim 1, wherein the top layer includes metal which is catalytic to the decomposition of the gas carrying the carbon or/and nitrogen atoms.

- 10 The metal layer protects the stainless steel surface from oxidation and acts as a catalytic surface for the decomposition of the gas. As a result, the process temperature can be kept below the temperature at which carbides and/or nitrides are formed, and the process can be finished within a reasonable period of time. After the thermo-chemical treatment, the catalytic metal layer can be removed to expose and repassivate the hardened stainless steel surface.
- 15

- When carbon atoms, nitrogen atoms or both diffuse into stainless steel, the metastable S-phase is formed. S-phase is also called "expanded austenite" and has carbon and/or nitrogen in a solid solution at an upper stable temperature of about 450°C
20 when it is nitrogen-stabilized, and at about 550°C when it is carbon-stabilized. Thus, the process according to the invention can be carried out at temperatures up to 450°C or 550°C to obtain S-phase.

- Until now, S-phase in stainless steel has almost only been obtained by plasma-assisted or ion implantation-based processes. Tests have established that the formation of S-phase at the surface does not negatively change the corrosion resistance of stainless steel. For nitrogen-stabilized S-phase an improvement of corrosion resistance can be obtained.
25

When stainless steel is treated with the method according to the invention, the hardness and wear resistance are improved considerably without the deterioration of the corrosion properties.

- 5 The ammonia synthesis, i.e. the production of NH₃ from H₂ and N₂, involves the use of a number of catalytic metals. Traditionally, the process is carried out at temperatures in the range 400°C – 700°C at high pressures (>300 atm) in the presence of a catalyst material. Gaseous nitriding is in principle the reverse process of the ammonia synthesis, where ammonia is dissociated on a metal surface producing N available for diffusion into the material to be nitrided. The conventional nitriding process is carried out within the same temperature interval as the ammonia synthesis process but at normal pressures. The catalytic metals available in the ammonia synthesis process are also found to promote the low-temperature catalytic reaction (ammonia dissociation) of the nitriding process. Known catalysts from the ammonia synthesis 10 process include Fe, Ni, Ru, Co, Pd among others.
- 15

According to an embodiment, the top layer includes one or more of the metals Fe, Ni, Ru, Co or Pd.

- 20 According to an embodiment of the invention, the case-hardening is a nitriding process which is carried out with a nitrogen containing gas below a temperature at which nitrides are produced, preferably below approximately 450°C.

- EP 0248431 B1 discloses a method where an austenitic stainless steel article is electroplated with iron before nitriding at 575°C for 2 hours. As mentioned before, chromium nitrides are formed at this temperature. As disclosed on page 4, lines 13 to 18 of EP 0248431 B1, only the valve shaft of a valve is nitrided. The valve disk (Ventilteller) is protected from nitriding by an oxide layer in order not to reduce the 25 corrosion resistance of the valve disk.

The same idea is followed with respect to carburizing, where the same catalytic metals are applicable also.

- 5 The material applied for the surface layer should include the well known materials from the ammonia synthesis process either as pure metals (single layer), as alloys, as a metal layer doped with other metals and as multi-layers.

- As an example, a stainless steel article could be provided with an iron layer and a
- 10 very thin ruthenium layer on the top of the iron layer.

Claims

1. A method of case-hardening a stainless steel article by means of gas including carbon and/or nitrogen, whereby carbon and/or nitrogen atoms diffuse through the surface of the article, the method including activating the surface of the article, applying a top layer on the activated surface to prevent repassivation, **characterised in that** the top layer includes metal which is catalytic to the decomposition of the gas.
2. A method according to claim 1, wherein the top layer includes one or more of the metals Fe, Ni, Ru, Co or Pd.
3. A method according to claim 1 or 2, wherein the case-hardening is a nitriding process which is carried out with a nitrogen-containing gas below a temperature at which nitrides are produced, preferably below approximately 450°C.
4. A method according to claim 1 or 2, wherein the case-hardening is carburizing with a carbon-containing gas, preferably CO, and where the top layer is free of Fe.
5. A method according to claim 4, wherein carburizing is carried out below a temperature at which carbides are produced, preferably below approximately 550°C, more preferably below approximately 510°C.
6. A method according to any of the preceding claims, wherein the top layer is a nickel layer.
7. A method according to claim 6, wherein the maximum average thickness of the nickel layer is 300 nanometer, preferably 200 nanometer.
8. A method according to claim 6 or 7, wherein the nickel layer is applied by a chemical or electrolytical plating process, e.g. by electro-plating in a Wood's nickel bath.

9. A method according to any of the preceding claims, wherein the article is of austenitic stainless steel.
- 5 10. A method according to any of the preceding claims, wherein the catalytic metal layer is only applied to parts of the surface of the stainless steel article.
11. A stainless steel article treated by a method according to any of the preceding claims.